

# Best Available Copy

## PATENT SPECIFICATION

NO DRAWINGS

Inventors: FRIEDRICH WOLF, HERMANN BEYER and UDO HADICKE

956,276



Date of Application and filing Complete Specification July 6, 1960.

No. 23704/60.

Complete Specification Published April 22, 1964.

© Crown Copyright 1964.

Index at acceptance: —C3 T(6D2, 6D4, 6F1, 6G7B, 6G7E)

International Classification:—C 08 g

### COMPLETE SPECIFICATION

#### Process for the Manufacture of Thermostable Organo Silicon Anion Exchangers

- We, VEB FARBFABRIK WOLFEN, a Corporation organised under the laws of the Eastern Zone of Germany, of Wolfen, Kreis Bitterfeld, Eastern Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 Anion exchangers based on synthetic resins of various compositions and prepared by condensation or polymerisation processes are known. Since the structure of the synthetic resin is organic the thermostability of these exchangers is relatively low and is generally reliable only up to about 70°C.
- Hitherto the only thermostable synthetic ion exchangers known have been cation-exchangers on a silicone base of which, for example, catalysts are made that are capable of exchanging hydrogen. A similar demand exists for thermostable anion-exchange in hot media.
- The present invention provides a process for the manufacture of such anion exchangers, and is based on the observation that such thermostable anion-exchangers are obtained by introducing amino groups of maximum basicity into the silicic acid molecule. Since direct Si—N bonds hydrolyse very readily, the bond must be formed through a carbon atom.
- Accordingly, the exchangers are produced by condensing an aminoalkyl siloxane or an aminoalkyl-alkoxysilane with silicic acid or with a alkylorthosilicate. To obtain the desired thermostability and to reduce the effect of steric hindrance, the organic residue should be as small as possible. Good results have been obtained for example with groupings of the following type:
- 45
- 50
- 55
- 60
- 65
- 70
- 75
- 80
- $$[\text{SiO}_{4-a} (\text{C}_b\text{H}_{2b}\text{N.R}_c\text{H}_{3-c})_a]^- [\text{y}]^+$$
- where a = 1—3, b = 1—6, c = 0—3, y = an anion.
- The process of the invention may be carried out for example by reacting a tertiary or quaternary amino alkylalkoxy silane or aminoalkylsiloxane with silica gel or silica jelly. The term "gel" herein is to be understood to mean a Xerogel, that is a product which is obtained by heating a jelly to a higher temperature. The jelly itself contains water and in the present case forms a water-glass solution on treatment with an acid. The compound containing the amino groups is allowed to diffuse into the gel or jelly and the whole is then condensed at an elevated temperature (50—150°C) with elimination of alcohol or water.
- The amino alkylsiloxanes are prepared in the known manner by chlorinating the alkyl groups of an alkylchlorosilane photochemically or with sulphuryl chloride in the presence of a catalyst, subsequent esterification of the Si—Cl groups with, preferably, a lower alcohol, amination with a primary, secondary or tertiary alkylamine, and hydrolysis of the aminoalkylalkoxysilane to an aminoalkylsiloxane.
- Instead of using silica gel or jelly a silicon tetraalkyl ester can be hydrolysed together with the aminoalkyl alkoxy silane and then condensed.
- According to a modification process of the invention silica gel is alkylated with an alkylchlorosilane, the alkyl radicals are chlorinated (photochemically or with sulphuryl chloride and a catalyst) and then aminated with the alkylamine.
- In the process of the invention the tertiary

# Best Available Copy

2

956,276

or quaternary aminoalkyl alkoxy silane is hydrolysed, or the starting material used is an aminoalkylsiloxane and the polycondensation is performed at an elevated temperature. This process furnishes a solid, porous silicone resin containing exchange-active amino groups.

The resulting products are yellow to brown silica gels having an anion-exchange capacity of 0.3 to about 1.0 mVal/g of anhydrous exchanger. The relative basicity is low (15—20% of 0.1N—NaOH). The range of thermostability is as high as 180—240°C.

The unit "mVal/g" means milliequivalent per gram and represents the total weight capacity of the exchanger i.e. it indicates how many milliequivalent ions per 1 gram of dry exchange material can be replaced.

The following Examples illustrate the invention:—

### EXAMPLE 1

50 grams of silica gel (grain size 0.5—1.25 mm) were dried at 120°C, covered with 80 grams of  $\alpha$ -diethyl-aminoethyl-triethoxy silane and kept for several days. The reaction mixture was periodically stirred and then dried for 6 hours at 120°C. The absorbent was activated with dilute sodium hydroxide solution and washed until it is neutral. Its exchange capacity amounted to 0.45 mVal/g, 30 its pour weight being 0.56 g./cc.

### EXAMPLE 2

200 grams of silica jelly were washed free from electrolyte and then freed from adherent water by means of methanol. The alcoholic jelly was covered with a solution of 20 grams of  $\alpha$ -diethylaminoethyl-triethoxysilane and 120 grams of absolute methanol and left for one day. The reaction mixture was periodically stirred and then dried for 6 hours at 120°C.

### EXAMPLE 3

50 grams of silica gel (grain size 0.5—2.5 mm.) were dried at 120°, introduced into a flask and covered with absolute chloroform. While stirring the mixture, 13.1 grams of ethyltrichlorosilane were added dropwise. Hydrogen chloride gas was evolved. The mixture was then refluxed for  $\frac{1}{2}$  hour, treated with 64 cc. of sulphuryl chloride and 0.1 gram of benzoyl peroxide and refluxed for 1 to 2 hours. The liquid was decanted and the gel heated with 250 cc. of diethylamine for 6 hours at 120—125°C in an autoclave. The product was activated with dilute sodium hydroxide solution and washed until neutral. The capacity 55 of the exchanger obtained in this manner amounted to 0.4 mVal/g.

### EXAMPLE 4

A mixture of 21 grams of silicon tetraethyl ester and 25 grams of diethylaminomethyl-triethoxysilane were hydrolysed with 12.6 grams of water with stirring and cooling. The reaction product was evaporated on a steam bath and the resulting yellow jelly was then shrunk and dried by heating at 120°C. The exchange capacity of the product amounted to 0.8 mVal/g.

### WHAT WE CLAIM IS:—

1. A process for the manufacture of a thermostable anion-exchanger, wherein an aminoalkylsiloxane or an aminoalkyl-alkoxy silane is condensed with silicic acid or with an alkylorthosilicate.

2. A process as claimed in Claim 1, wherein the aminoalkyl silicon compound is reacted with silica gel or jelly.

3. A process as claimed in Claim 1 or 2 in which the compound containing the amino alkyl groups is allowed to diffuse into the silica gel or silica jelly and then condensed at an elevated temperature with elimination of alcohol or water.

4. A process as claimed in Claim 3, wherein the condensation takes place at 50°C—150°C.

5. A process as claimed in Claim 1, wherein a silicon tetraalkyl ester is hydrolysed together with an aminoalkylalkoxy silane and then condensed.

6. A modification of the process claimed in Claim 1, wherein silica gel is alkylated with alkylchlorosilane, and the alkyl radicals are chlorinated and then aminated with an alkylamine.

7. A process for the manufacture of a thermostable anion-exchanger conducted substantially as described in any one of the Examples herein.

8. Thermostable anion-exchangers whenever made by the process claimed in any one of Claims 1—7.

9. Thermostable anion exchangers containing a grouping of the type



where a = 1—3, b = 1—6, c = 0—3, y = anion whenever made by the process claimed in any one of Claims 1—7.

ABEL & IMRAY,  
Chartered Patent Agents,  
Quality House, Quality Court,  
Chancery Lane, London, W.C.2.